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Recent Developments in X-Rays

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RECENT DEVELOPMENTS IN X-RAYS

by

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INTRODUCTION

The Geissler tube is the pioneer of many wonderful discoveries and speculations. The close study given to the discharge tube has been repaid by the manifold achievements of scientists following Roentgen's investigations. Many theories have been offered to account for the nature of X-rays though none have satisfactorily explained the phenomena. With the discovery that they can be reflected and diffracted from crystals, increased interest has been shown in the attempt to reconcile certain theories with the observed facts. The classical electron theory and the quantum principles are now used though they appear to conflict with each other in certain phases such as scattering of rays and fluorescence. Neither of the theories account for all the observed phenomena. The study of Roentgen rays is a profitable field for learning the connection between these two points of view. One also acquires some knowledge of the atom and of crystal structure. Perhaps the study is of most interest in identifying X-rays with light and seeing the relationship established between the X-ray spectrum and the order of an element in the periodic table. While mention was made of these the principal object in this research was to summarize briefly the work of a few noted scientists in the spectroscopy of X-rays. Nothing has been said of X-ray diffraction apparatus. A complete description of such apparatus may be found in the General Electric Review of February 1926.

HISTORY

In the autumn of 1895 Prof. Wilhelm K. Roentgen[1] of Wurtzburg, Bavaria, while experimenting with the vacuum tubes of Lenard discovered a new form of radiation which he called X-rays. In searching for invisible light rays, he turned on a low pressure discharge tube enclosed in stout black paper. He noticed that a fluorescent screen lying nearby shone out brightly. He traced the source to the discharge tube. Previous to this English physicists had noticed a fogging of unopened photographic plates in the neighborhood of a Crookes tube but they were unable to account for the phenomenon. In 1896 J. J. Thomson and others found that X-rays shared with cathode rays, and ultra-violet light, the property of ionizing gases. He also showed that when X-rays strike metallic plates new rays are set up at the metal surfaces, having penetrating properties peculiar to the metal from which they arise and independent of the penetration of the rays producing them.

Roentgen discovered how to produce "hard" and "soft" rays, and showed that the rays were not deviated in a strong magnetic field. He attempted to show interference phenomena but without result. Different attempts were made by Haga and Wind in 1902 and later attempts were made by Walter and Pohl, but the effects observed were small and not especially convincing. The quantum theory of radiation had succeeded in determining the order of magnitude of the wave length of X-rays, about 10^{-9} cm., while the atomic distances are of the order of 10^{-8} cm. This led Laue to believe that the orderly arranged space lattice of a crystal would give rise to interference phenomena with X-rays. Experiments in this line carried

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1) A. Rt. R. (Feb. 1899)_ (Archives of Rontgen Ray).

out by Friedrich and Knipping[2] proved the truth of Laue's conception. It also showed that X-rays and light are identical in nature, the difference being in wave length. Laue's idea gave a better method for the study of X-rays and crystal structure. W. H. and W. L. Bragg showed that a natural surface, can under certain conditions reflect X-rays in part according to same laws which obtain in ordinary optical reflection. The Bragg equation is deduced from a modified form of Laue's theory. Later, Sieghahn has shown the Bragg equation, $\lambda = 2d \sin\theta$ is not valid in measurements that require great precision.

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2) Annalen der Physik

LAUE'S THEORY

Prof. M. Laue of Munich believed that X-rays were short rays of same nature as light rays with wave lengths of an atomic order of magnitude. He conceived the idea that the regular grouping of the atoms in a crystal should be capable of producing interference effects with the X-rays. In a crystal, like atoms form a space lattice independent of other atoms present. Since the atoms repeat themselves at definite intervals Laue held that they should be capable of acting as a three dimension diffraction grating for rays of suitably short wave lengths. Assume an elementary cube with the atoms arranged at the corners. The X-rays on passing through the cube influence the atoms enroute, and a secondary ray spreads from each atom as a wave passes over it. Take axis of reference on sides of cube with a corner of the cube as origin at center of one of the atoms. Now if a beam enters the cube in the direction of the Z axis, there will be some particular direction in which the waves from the various atoms shall be in phase. Call this direction OP. then (1) $a\alpha = h\lambda$; (2) $a\beta = h_2\lambda$; (3) $a(1-\gamma) = h_3\lambda$, where a is the distance between neighboring atoms (one side of the cube) λ is the wave length of the X-rays, and h_1, h_2, h_3 are integers representing the number of complete wave lengths that the waves, from corners of cube nearest O, are ahead of the wave from O. It is evident that there are a number of other points of maximum intensity situated like P with reference to the Z axis. If a photographic plate is placed to receive the X-rays, there will appear a group of spots of four fold symmetry. Laue's theory was tested out by Friedrich and Knipping by arranging that a parallel beam of X-rays traversing a crystal should be received on a photographic plate, so that

any directions showing interference maxima would be registered as spots. The results from the first trial verified the theory.

The X-rays emitted from the bulb were cut down by lead stops to a narrow beam which was directed on the crystal. The plate showed an intense undeflected spot, other spots grouped around it in a symmetrical order. By changing the distance of the plate from the crystal, the spots moved in or out from the center. By rotating the crystal into a new position with respect to the primary beam, the pattern on the plate was affected. Since the direction cosines α, β, γ have the relation $\alpha^2+\beta^2+\gamma^2=1$ there is only one value which will satisfy the equations for each spot. It was found that certain spots associated with simple values of h_1, h_2 and h_3 were absent and Laue sought to explain this by assuming that the primary beam was made up of a limited number of homogeneous constituents. Laue was able to account for all the spots in the photograph by assuming the existence of five different wave lengths in the incident beam. The explanation was not entirely satisfactory.

A zinc-blende crystal belongs to the cubic system and in this there are three elementary forms of cubic symmetry, namely:

(1) points at each corner of the elementary cube,

(2) points at each corner and one at the center, and

(3) points at the corners and at the centers of the faces.

Laue assumed zinc-blende to belong to the first system, but W. L. Bragg chose the third point of view. Making this assumption it is necessary to obtain corresponding conditions for the center-face atoms so that their wavelets shall be in phase with those from the corner atoms. The difference in phase between wavelets from a corner atom and mid-face atom must be a whole number of wave lengths to give maximum interference along the

resultant. It follows the numbers must be both odd or even. This explains why all the spots were not shown on the plate. Bragg concluded that the X-rays utilised in this particular Laue pattern formed a continuous spectrum.

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W. L. Bragg's Theory and Reflection of Crystals[1]

As before stated Bragg concluded that an incident beam contained every possible wave length over a wide range and thus formed a continuous spectrum. When such a beam falls on a crystal, assuming that it strikes a system of parallel planes of atoms, a small amount of energy is reflected by each plane. A wave front is formed by wavelets sent out by the individual atoms in the plane. Let d equal the distance between successive planes and θ equal the glancing angle of the beam, the train of waves reflected from the different planes in the system will follow each other at intervals of $2d \sin\theta$. If the wave length is such that this distance is equal to a whole number of wave lengths, the waves will be reinforced. We will get a maximum interference in that direction. When a beam contains all possible wave lengths a particular system of planes in the crystal will pick out certain wave lengths. Using all the various systems of planes in the crystal we may resolve a beam into its constituents. By altering the angle of incidence different wave lengths may be selected to form interference maxima. If only certain wave lengths were present in the beam then as the crystal is tilted spots would appear and disappear on the photographic plate but such is not the case. The same spots may be traced continuously across the plate. Some spots quite dim when the crystal is in one position becomes more intense in another position because its new wave length now coincides with the maximum.

At C. T. R. Wilson's suggestion Bragg was led to ascertain whether X-rays were regularly reflected from cleavage planes in crystals. An

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1) Bragg - X-ray and Crystal Structure, Chapter 2.

experiment performed by using mica gave very successful results. Only a few minutes exposure was necessary to give a visible impression on a photographic plate. If a train of X-rays of the same wave lengths falls on the crystal, reflection will only take place when the glancing angle has certain values such as $\lambda = 2d \sin\theta_1$, $2\lambda = 2d \sin\theta_2$ where d is the distance apart of the planes. The reflection θ_1 gives the first order spectrum, θ_2 the second, etc. With these relations existing between λ and d by employing the same crystal face the wave lengths of different monochromatic X-rays can be compared. By using the same wave length, the spacing d can be compared for different crystals or different faces of the same crystal. With monochromatic rays it is at only a few special angles that reflection can be detected. With a mixture of monochromatic and general radiation, if the strength of the reflected beam is plotted against the glancing angle, there will be a smooth background of white radiation on which are superposed "peaks" corresponding to the monochromatic spectrum "lines". The position and form of the peaks depend on the material of the anticathode of which they are characteristic. The reflection of the monochromatic vibration gives more information about the crystal structure than the reflection of the white radiation. Bragg and his son devised the X-ray spectrometer[1] in which the crystal is used as a reflection grating. A Coolidge[2] tube of special form is enclosed in a wooden box coated with lead. The rays pass through two slits, one in the box, the other near the crystal which is mounted on a revolving table carrying an arm. At the end of the arm is a vernier working in conjunction with a graduated circle. The reflected

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1) Bragg - X-ray and Crystal Structure, Chapter 3.
2) Phys. Rev. Dec. 1913

pencil passes into an ionization chamber which revolves about the same vertical axis as the crystal chamber. The chamber is filled with a gas which absorbs the X-rays strongly, and so yields a large ionization current. The ionization chamber is insulated and kept at a high potential. In studying crystal structure the essential thing is the angle of reflection and it is determined directly by the angular setting of the crystal table. The angular setting of the ionization table is of secondary importance. The crystal is assumed to be so small that portions of it concerned in the two reflections are essentially the same. When the spectrometer is used to study X-ray spectra the crystal is merely an essential portion of the spectrometer. The spacing of the reflecting plane should be of convenient magnitude and the reflection should be intense.

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THE THEORY OF X-RAY SPECTRA

One of the postulates of Bohr's theory[1] is that when a change takes place in the electron system of an atom, resulting in a change of energy from W_1 to W_2 the atom gives off a quantity of energy $W_1 - W_2$ as monochromatic electromagnetic radiation of frequency ν which is determined by the equation $\nu = \frac{W_1 - W_2}{h}$. There are two principal reasons given to show that the changes which give rise to X-ray spectra take place in the inner region of the envelope of electrons. The first is that the X-ray spectrum is an atomic property which is quite independent of the chemical nature of the element; the other is that the frequencies involved in X-ray spectra are very great in comparison to those of optical spectra, and are therefore associated with correspondingly large energy changes which involve electron orbits of high energy content. Since X-ray spectra differ very slightly in passing from one element to another through the whole atomic system, we may infer that the inner portions of the atoms are built up on very much the same plan. The regular increase of frequencies with increasing nuclear charge is an evident consequence of the increase of the intensity of the electric field within the atom. The wide separation of the spectrum lines shows that there is a correspondingly large energy difference between certain inner electron groups and those still nearer the nucleus. The innermost group is called the K group, the next the L group, etc. If an electron is missing in the K group and its place is filled by an electron from the L group, the energy change is known as a K radiation and the most probable transition corresponds to the strongest line of the K series, the $K\alpha$ line. If the electron comes

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1) Data Relating to X-Ray Spectra - Wm. Duane.

from the M group the result is the radiation of the $K\beta$ line. The γ line is due to electrons falling from the fourth orbit and from all orbits outside it to the first. There are two methods of determining the energy difference between the level of the normal state and the K level. One consists in determining the critical potential for the K series, by which just enough energy is given to the impinging electron to enable it, on colliding with an atom, to eject an electron from the K group. The other method is based on the determination of the frequency of the K absorption discontinuity.

It is rather difficult to determine the excitation voltages necessary to give the electrons these high velocities, and hence in only a few cases has the voltages been measured experimentally with the required degree of accuracy. The second method is easily carried out and the absorption spectra concerned have now been extensively investigated. A third method is provided by the phenomena of corpuscular secondary radiation and gives promise of being as accurate as other methods.

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SECONDARY X-RAYS

Secondary X-rays mean any radiation of the X-ray type excited by the passage through matter of primary X-rays.

(a) The scattering of such rays means the radiation emitted by the electrons in matter due to accelerations to which they are directly subjected by the primary rays.

(b) Fluorescent radiation is radiation of the energy absorbed from the primary beam and stored temporarily in the kinetic and potential energies of the electrons.

It is sometimes difficult to distinguish between these two types of secondary radiation. Two methods of making this distinction have been employed. The first depends upon Stoke's law, according to which the wave-length of the fluorescent radiation should be greater than that of the primary which excites it. The truly scattered rays are of the same wave length as the primary rays. It is possible by a comparative study of the absorption of the primary and secondary rays to determine what part of secondary beam is identical in character with the primary beam. A more certain way is to compare the spectrum of the secondary with that of the primary X-rays. If the primary rays are homogeneous, and if the electrons traversed are at rest the scattered beam will be homogeneous and of the same wave length, whereas the fluorescent rays will differ in wave-length from the primary.

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THE SCATTERING OF X-RAYS

1. By Electrons Acting as Point Charges

Every electron in matter traversed by primary X-rays will be subject to accelerations and will therefore radiate energy. On the basis of the assumptions: that (1) the classical electrodynamics is applicable, that (2) the forces of constraint on each electron in matter are negligible, that (3) the electrons scatter independently of each other and that (4) the size of the electron is negligible, J. J. Thomson showed[1] that the intensity of the X-rays scattered per unit volume of matter traversed by the X-rays, to a point at distance L and at an angle θ with the primary beam, is $I_s = N I_0 = I \frac{N_m e^4 (1 + \cos^2 \theta)}{2 m^2 L^2 c^4}$ (1) where N is the number of negative electrons in the atom, n the number of atoms per unit volume, I_0 is the intensity of the scattered beam due to each electron, I the intensity of the primary beam e and m the charge and mass, and c the velocity of light. Using moderately soft X-rays and carbon for the radiating material, Barkla and Ayers[2] found that the factor $1 + \cos^2 \theta$ accounted satisfactorily for the relative intensity of the secondary rays at angles θ greater than 40°, and later Barkla showed that this formula expressed quantitatively the intensity of the secondary rays at 90° from the lighter elements if N is taken as about half the atomic weight. The assumptions employed by Thomson therefore seem to be justified.[3]

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1) J. J. Thomson, "Conduction of Electricity through Gases, 2nd Ed.
2) Phil. Mag. 21, 275 (1911)
3) H. H. Compton, Phys. Review, 18, 96 (1921)

2. Scattering by Groups of Electrons.

Using soft X-rays and scattering material of higher atomic weight it was found that the rays scattered[1] in the forward direction are more intense than those scattered backward. The excess of the scattering over the theoretical value increases with the atomic number of the scattering material and with the wave length of the X-rays employed. This is clearly shown by certain experiments due to Barkla and Dunlop. The relative mass scattering by the different elements should be proportional to the number of electrons per gram, that is, I/I_{Al} should be nearly unity. It appears from these experiments that this relation may be exact for sufficiently short wave-lengths, but does not hold for the heavier elements at moderate wave lengths. Any effect due to the forces of constraint on the scattering electrons would be to modify the amplitude of their motion, thus changing the intensity equally in all directions, and could not account for asymmetrical scattering in the forward and backward directions. If the size of the electron were appreciable, the difference in phase of the rays scattered by its different parts would result in a reduced instead of an increased intensity. Glocker and Kaupp[2] have recently calculated the scattering of atoms composed of two or three coplaner rings of electrons revolving at different speeds. This confirms the conclusion which had been reached by Compton, that the scattering by groups of electrons in the atom depends principally upon the distance of the electrons from the center, and only slightly upon their spatial distribution. If sufficiently refined measurements of the scattering can be made, it may be possible to distinguish between the spatial arrangements considered in the different formulae. Figures show

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2) Ann. d. Phys. 64, 541 (1921)
1) Phil. Mag. 31, 229 (1916)

that by taking into account the phase relations between rays from the various electrons in the atoms, a satisfactory explanation may be given of the excess scattering of soft X-rays by heavy atoms.

3. Scattering by Electrons of Appreciable Dimensions

Ishino has found[1] that the total secondary gamma radiation averaged over different angles is less than one fourth of the energy calculated by expression (1) for the scattered radiation. Barkla and White pointed out that similar reduced scattering occurs when hard X-rays are used, when they observed a total absorption in paraffin less than the energy which should be lost according to Thomson's theory due to scattering alone. These results are supported and extended by H. H. Compton's measurements[2] of the part of the secondary radiation which has the same wave length as the primary X-rays. On the view that these rays only are truly scattered his data indicates that at small angles with the primary beam the scattering of hard X-rays by light elements is approximately that given by Thomson's expression(1). At larger angles however the intensity of the scattered beam is decidedly less than the theoretical value, the difference increasing for shorter wave lengths. For hard gamma rays he finds the rays at large angles less than .001 of Thomson's theoretical value. It is obvious that if the electron is comparable in diameter with the wave lengths of the X-rays, partial interference will occur between the rays scattered from its different parts, reducing the intensity of the scattered beam, and that this interference will be more nearly complete for rays scattered at the larger angles.

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1) Phil. Mag. 33, 129 (1917)
2) Phil. Mag. 41, 749 (1921)

4. Scattering by Small Crystals.

Debye and Scherrer pointed out that in a random assemblage of crystals some will be so oriented as to reflect X-rays from every plane which can be drawn parallel to layers of atoms in the crystal. Every possible layer of atoms gives rise to a reflected beam which may be recorded on a photographic plate. Debye and Scherrer and especially Hull have made extensive applications of this method in determining the arrangement of the atoms in substances which cannot readily be obtained in the form of large crystals. For investigations of the arrangement of the atoms in crystals, in which the different angles θ at which scattered rays appear are of first importance, the scattering of X-rays by powdered crystals has been studied only by the photographic method.

W. H. Bragg has coated a flat plate with a layer of the powdered crystals and has used this plate in place of the crystal of an X-ray spectrometer. When the two arms of the spectrometer are equal, X-rays are scattered into the slit of the ionization chamber from all parts of the plate at approximately the angle θ_1.[1] Work with powdered crystals has an advantage over similar work on the reflection from large crystals in that the absorption coefficient involved is directly measureable. The particles are arranged at random so that their axes are oriented in all directions. The substance to be examined is irradiated by homogeneous X-rays of wave length λ. If a photographic plate is placed so as to intercept the reflected rays, all beams corresponding to any given face and order of reflection fall on the plate at some position on a circle, with the point of incidence of the transmitted beam as a

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1) Braggs "X-rays and Crystal Structure," p. 26.

center, and are recorded as a halo surrounding the central image. Friedrich published results of experiments in which he had obtained diffraction rings by passing a beam of X-rays through a plate of paraffin wax. The significance of this experiment was not fully realized at the time.

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SCATTERING BY LIQUID

Substances to which it does not appear possible to attribute a crystallive structure in the ordinary sense appear to have the power of giving rise to diffraction rings. Debye's theory predicts rings when a beam of X-rays traverses an irregular assemblage of atoms on account of the fact that in each atom the distribution of the electrons has a structure. Such phenomena can be observed when X-rays pass through isotropic liquids like benzene. Rings have been obtained with various other liquids, mercury, methyl iodide, etc., and with some mixtures. Debierne[1] has explained the result by assuming that diffraction centers either atoms or molecules, exist in these liquids, which though distributed at random, satisfy the condition that neighboring centers have always the same distance between them, like the centers of small spheres in contact. Considering two neighboring centers in a position with respect to the direction of the incident beam, the interference that takes place will cause addition of amplitudes.taking place in a direction making an angle with the ray which can easily be calculated. The minimum value of the angle is given by $\sin \alpha/2 = \lambda/2a$, λ being the wave-length of the radiation and a the fixed distance between the centers.

Keesom and de Smedt[2] have studied interference figures presented by certain liquids and liquified gases and give the following values for a between diffracting molecules of substances. Oxygen, 4.0A°; Argon, 4.0A°; Benzene 6.0A°; Water 3.7; Ethyl alcohol 4.9 A°.

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1) Comptus Rendus, 1921, P. 140 (1922)
2) Ann. de la Soc. Scient de Bruxelles 1922 p. 338.

THE ABSORPTION OF X-RAYS

When a thin sheet of any substance is placed in the path of a homogeneous beam of X-rays the intensity of the beam is diminished and the intensity of the radiation after penetrating to a depth x is $I = I_0 e^{-\mu x}$ where I is the intensity at the surface., u is called the "absorption coefficient" and μ/ρ the mass absorption coefficient, the fraction of a beam 1 cm. in cross section absorbed per gram of substance traversed; and μ/ν, the atomic absorption coefficient where ν is the number of atoms per cm. is the fraction of such a beam absorbed by each atom of the substance. The beam of X-rays must be narrow, and the opening into the ionization chamber small so that no appreciable amount of secondary rays will pass into the ionization chamber. If the arrangement is such that only an inappreciable fraction of the scattered radiation enters the measuring chamber the coefficient u is the sum of two distinct coefficients and we have the equation $\mu = \sigma + \tau$ where σ measuresthe scattering and τ measures the actual absorption.

There is a rapid increase in absorption with increase of wave length. There are, however, certain critical regions in which there is a sudden decrease in absorption for a slight increase in wave length. The wave lengths at which these sudden changes take place are known as critical absorption wave lengths. If the wave length of the radiation is shorter than the shortest of these critical wave lengths, the complete X-ray spectrum of the absorbing element is excited including the characteristic K-radiation. A slightly longer wave will excite only the characteristic fluorescent radiations L, M, etc. but not that of

the K-type. There are at least three critical absorption wave-lengths associated with the L series, at each of which a separate portion of the emission spectrum of the L series disappears. The critical absorption wave-length associated with any X-ray spectral series is very slightly shorter than the shortest emission wave length of the series. This means that any element is especially transparent to its own characteristic radiation.

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DEPENDENCE OF ABSORPTION ON CHEMICAL COMBINATION OF THE ELEMENT.

It has recently been found that the chemical combination of the atom influences X-ray spectra to a certain extent. Bergengren discovered the first indicationsof such an influence and from his limited investigation concluded that the basis of this difference is in the allotropic modification of the element. Lindh made the discovery that the X-ray absorption spectrum of an element often varies greatly as to its chemical state in the compound investigated. Chlorine, sulphur and phosphorus showed this peculiarity. In the study of absorption spectra in the region of long wave lengths we must consider that such spectra represent no purely atomic property but that they depend on the form of chemical combination in which the element may happen to be. The absorption spectrum obtained for an element in a homogeneous compound shows, generally, in addition to the absorption discontinuity certain brighter and darker lines on the short wave length side. In some cases these lines are more strongly developed than in others. Results of Lindh's measurements show on the whole, that the absorption spectra of all compounds, in which the valency of chlorine is the same, are identical. HCl is apparently an exception, the absorption wave length being greater than for other monovalent compounds. Free chlorine occupies an entirely separate position with considerably greater wave length of the absorption edge. Tetravalent and hexavalent compounds of sulphur were studied, organic as well as inorganic. The two allotropic modifications showed no appreciable difference in their absorption spectra. The sulphides exhibit

differences in the position of the principal absorption edge, which lie outside the limits of error. In a long series of sulphates with various metal atoms no variation was found in the principal limit. Secondary limits were measured only for Li, Na and K, but in the case of these three there was a pronounced and rather regular increase of wave length of the secondary limit with the atomic number of the metallic atom.

A comparison of averages for inorganic and organic compounds shows that in the latter the absorption edges for tetravalent and hexavalent sulphur be about 6 X. U. farther towards greater wave lengths. The most significant fact revealed is that the absorption spectra of divalent sulphur are in general of the simple edge type, while in the tetravalent and hexavalent group distinct absorption hues are found. While Lindh's study of phosphorus clarified the work of Bergengren a more extensive study of the absorption spectra of this element has recently been carried out by P. Stelling.

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EMISSION SPECTRA

Kaye has shown that the characteristic radiation is preserved when the element in question is made the anticathode in the X-ray tube. Since much greater intensity may be obtained in this way, the method is used almost exclusively for the production of characteristic radiation. Barkla's method of secondary radiation may be used in spectrographic work as demonstrated by DeBroglie. The characteristic radiations from Pt, Os, Ir, Pd and Rh were investigated by Bragg and were found to be separated into a number of sharp spectral lines. Moseley investigated a series of successive elements in the periodic system employing the photographic method. The most important result of his investigation is the remarkable fact that the spectra shift uniformly according to a simple law when we pass from one element to the next in the periodic system. Later Moseley extended his earlier study of the K series to the L series and found that all the elements from Zr to Au were subject to relations such as he had previously found for a portion of the K series. Barkla in 1916, believed he had found evidence of a harder series of lines than the K series, which he denoted by J. Siegbahn and others have been unable to find any trace of an emission spectrum in the wave length region where, according to Barkla, the J radiation should be. The X-ray spectra of the elements in the wave length region from about .1 A^0 to 13 A^0 may be divided into four groups, the K, L, M, N series; each group being divided into a number of more or less sharp spectral lines. Regions between these groups seem to be devoid of lines. Photographs of the spectra of adjacent elements show that each group retains its general appearance

with only small changes from element to element. A line is merely displaced towards shorter wave lengths when we pass from a lighter to a heavier element. Every substance emits independently a continuous radiation whether it is excited to the emission of X-rays by cathode ray impacts, or whether it is caused to give off its characteristic radiation by exposure to primary X-rays as in Barkla's method.

THE APPLICATION OF THE QUANTUM THEORY TO X-RAYS

The quantum theory was first applied to black body radiation. It is assumed that all matter contains large numbers of vibrators which can emit ether waves of different frequencies, but only spasmodically and in such a way that the quantity of energy emitted is an exact multiple of a certain unit or quantum. The amount increases with increase in frequency of vibration or $\epsilon = h\nu$ where h is Planck's constant[1] and is equal to 6.5 10^{-27} erg. sec. The generation of secondary corpuscular rays and photoelectrons is due to a quantum giving up some or all of its energy to an electron. The maximum frequency of the independent radiation generated in an X-ray bulb can be calculated from the equation $Ve = h\nu$ where V is the voltage and e is the electronic charge. The quantum theory is inadequate when applied to the scattering of radiation. Consider the case where $\nu > Ve/2h$, so that not more than one quantum of energy of this frequency can be radiated at the impact of each electron. The resulting X-ray when scattered by matter shows the phenomenon of excess scattering. This can be accounted for by the fact that the incident X-ray excites secondary radiation of the same frequency from several electrons in the same atom, with the result that these radiations cooperate in the forward direction and partially interfere with each other at larger angles with the incident beam. If it is assumed that each electron both absorbs and emits radiation in quanta, the primary ray can excite radiation from only one electron, and these interference effects become inexplicable. The several quanta might not all be radiated by electrons in the same atom and would not account for the observed interference

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1) X-rays by Kaye, p. 268

effects. In reflection of X-rays by crystals in order to account for the appearance of the reflected beam as a sharp line it is necessary to suppose that a large number of electrons in the crystal emit radiation in their proper phases when excited by a single quantum of incident radiation. The interference phenomena occurring are inconsistent with the view that an electron always emits scattered radiation in quanta. Experiments with the Michelson interferometer leads to the conclusion that radiation may be absorbed in amounts less than a quantum. One might conclude from this that radiation occurs in waves spreading throughout space in accord with the usual electrical theory. Experiments, however, show that the wave length of the scattered X-ray is greater than that of the incident ray[1]. This was explained on the ground that the radiation was received and emitted by each scattering electron in discrete quanta. DeBroghe's and Ellis' experiments[2] show that each photoelectron leaves its normal position in the atom with a kinetic energy hv. Duane and Hunt's experiments indicate that if the whole kinetic energy of a cathode ray is transformed to radiation at a single impact, then $E = hv$. A similar relation expresses quantitatively the frequency of the rays emitted as an electron falls from one energy level to another within the atom. It appears then that the quantum law may describe a reversible mechanism whereby energy may be interchanged between radiation and the kinetic energy of an electron. In the fluorescent absorption of X-rays, the energy absorbed appears again as the kinetic energy of the photoelectrons. The energy dissipated in scattering is not transformed in this manner and has no necessary dependence upon the quantum mechanism.

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1) Bragg X-rays and Crystal Structure, p. 297.
2) Proc. Roy. Soc., 1921, 29 p. 261

INDEX OF REFRACTION

Darwin[1] predicted that an X-ray beam would travel with a velocity slightly different from that in a vacuum and estimated the refractive index to differ from unity by one part in a million. The existence of the refractive index has been demonstrated by Compton. A very fine beam of X-rays is allowed to fall at a small glancing angle on a glass plate. The rays coming from the glass plate pass through a fine slit to an ionization chamber. The slit could be adjusted so as to admit rays making any given angle with the primary beam. By setting the slit for a given angle and turning the glass plate, he was able to show that a sharply defined maximum in the effect existed when the glass plate was set as to give specular reflection of the beam of X-rays, and that the reflection for small angles was almost total. On analyzing the reflected radiation by an X-ray spectrometer, he was able to measure the critical angle for definite wave lengths

A test of the refraction of homogeneous X-rays has been made by Webster and Clark[2]. They found that the refractive index for the different K lines of rhodium, transmitted by a rhodium prism, differed from unity by less than about 3×10^{-4}.

According to Lorenz[3], if the frequency ν of the radiation transmitted by a substance is high compared with the natural frequency of the electrons in the substance, its index of refraction $\mu = 1 - \frac{n e^2}{2\pi m \nu^2}$ where n is the number of electrons per unit volume, and e and m represent the charge and mass respectively. If the number of effective electrons

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1) Phil. Mag., 27, p. 320, 1914.
2) Phys. Rev. 8, 528 (1916)
3) The Theory of Electrons, 2nd Ed., p. 149.

per atom is assumed equal to the atomic number, the above equation gives a moderately accurate means of measuring the wave length, which is independent of crystalline grating space and of the quantum hypothesis. Since the refractive index depends only upon the number of electrons per unit volume, X-ray refraction measurements afford a valuable confirmation of the estimates of the wave length of X-rays and of the number of electrons in the atoms.

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INVALIDITY OF BRAGG'S EQUATION

Stenstrom has observed that for wave-lengths greater than about 3 Å. U. reflected from crystals of sugar and gypsum $n\lambda = 2d\sin\theta$ does not give accurately the angles of reflection. The fact that the law is not strictly true seems to have been pointed out first by Darwin. Knowing the index of refraction of the crystal, the true wave length can be calculated from the formula $\lambda = \frac{2d\sin\theta}{n}\left(1 - \frac{1-\mu}{\sin^2\theta}\right)$. Duane and Patterson and Siegbahn have noticed that even with ordinary X-rays the wave lengths observed in different orders do not agree. Bragg's law, $n\lambda = 2d\sin\theta$ will hold exactly for the glancing angle θ' of the rays inside a crystal, but not for the angle θ which the same rays make before incidence and on imergence.

USE OF X-RAYS IN DISCOVERY OF NEW ELEMENTS

It has been found that X-ray line spectra provide a method for analysis of the elements. The X-ray spectra are simple in comparison with optical spectra and are not influenced to any extent by the chemical state of the atom emitting them. Nonnack and Tacke announced the discovery, 1925, of two new elements with atomic numbers 42 and 75 which they called Masurium and Rhenium respectively. Moseley established the relationship between the X-ray spectrum and the order of an element in the periodic table. The method used was to plot the atomic number against the square root of the frequency of the X-ray. The points for the different elements were found to lie on a straight line. From this it was concluded that the wave length of the X-ray is inversely proportional to $(N-a^2)$ where N is the atomic number and a is a constant. There are still some gaps left in the periodic table to be filled in but the relationship of the elements to each other leads one to be assured that elements for the gaps, exist and will in time be discovered. The atomic number is seen to agree closely with the number of positive charges carried by the nucleus of the atom. It is also stated that the wave-length of a characteristic radiation depends directly on the magnitude of the nuclear charge.

Bohr has developed Rutherford's theory of the constitution of the atom and linked it up quantitatively with the with the quantum theory and Moseley's experimental results. Moseley's work has been carried further by Sieghbahn in extending the K series down to *Na* and the L series down to *Zn* and up to U. For the long wave lengths of X-rays the vacuum spectrometer was used. Siegbahn points out that a variation

in potential, of slight extent, produces a differential action and strongly affects the relative intensities of the spectral lines emitted from the different elements on the anticathode. Only when the elements have about the same atomic number in the periodic table, and the potential is considerably higher than the minimum potential necessary to excite the characteristic rays of the elements, is quantitative estimation possible by comparison of the intensities of the spectral lines.

X-ray spectra have settled the order of the rare earths by clearly demonstrating which substances are elements, by confirming the separation by Urbain of the old ytterbium into neoytterbium and lutecium and by verifying the elementary nature of thulium. Coster and von Hevesy have been able to show that the minerals containing zirconium also contain a very appreciable proportion of a new element. The new element is identical with the celtium of Urbain and Danvillier. Illinium, a new element, has been discovered by Hopkins. There are yet two elements to discover. Success must be obtained soon, since the chemical group to which the unknown elements belong and the region of the spectrum in which their lines must be sought are known by means of the periodic table and Moseley's law respectively.

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INDUSTRIAL APPLICATIONS OF X-RAYS

On account of the large effects produced by relatively small amounts of energy, X-rays may acquire great importance in production of organic compounds by its trigger action in causing a chemical change to take place.

An account is given[1] where a brass cell containing cyclo hexanol was subjected to X-rays and afterwards opened. The colorless liquid had turned to greenish-blue. An analysis showed that .1 gram of cu had gone into solution, the amount of energy involved being very small.

X-rays are used to detect flaws, blow-holes, or bad welds in metals where there is no adequate mechanical test available. Uneven distribution of metals in alloys[2] shows a streaky or patchy radiograph, also poor union between rubber and fabric in tire manufacture is shown by X-rays.

The makers of electrical insulators find X-rays invaluable for detecting the presence of foreign bodies and in the manufacture of optical glass, the fire clay pots were tested by X-rays for detecting iron and other impurities in the clay.

Kaye shows how modern paintings may be detected from the old. In a modern picture the sizing is very commonly more opaque than the pigments but in the pictures of the old masters the reverse condition is true. With a little experience the X-rays can be successfully used as a means of identifying a modern fake or detecting alterations to an

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1) Sc. Am. Sept. 1923.
2) Bragg--X-rays and Crystal Structure p. 295.

old picture. Dr. Heilbron of Amsterdam and Dr. Cheron of Paris have done a lot of work along this line. A Flemish panel attributed to van Ostade, and showing a part of country dancers was X-rayed. The radiograph revealed a farm yard scene. The panel was found to be modern since practically all its colors are transparent to the rays. The present limitations of industrial radiography are largely those prescribed by equipment and technique. The work of Bragg has given information concerning the arrangement of individual atoms in crystals. The study has thrown new light on the nature of cohesion, chemical valence, etc. The study of the intensity of X-ray spectra can furnish definite information concerning the arrangement of the electrons in atoms. Compton has shown that a change of wave length occurs when X-rays are scattered, which is all right according to the quantum theory but does not satisfy the wave theory. Kaye points out that evidence indicates that both theories are true simultaneously, and that this is the riddle of modern physics.

BIBLIOGRAPHY

A. Rt. R. (Feb. 1899) Archives of Routgen Ray.

Annalen der Physik

Bragg - Xray and Crystal Structure, Chapter II.

Bragg - X-ray and Crystal Structure, Chapter III.

Phys. Rev., Dec. 1913.

Data Relating to X-ray Spectra - Wm. Duane.

J. J. Thomson - Conduction of Electricity through Gases, 2nd Ed.

Phil. Mag. 21, 275 (1911)

Am. d. Phys. 64, 541 (1921)

Phil. Mag. 31, 229 (1916)

Phil. Mag. 33, 129 (1917)

Phil. Mag. 41, 749 (1921)

Bragg X-ray and Crystal Structure p. 26.

Comptus Rendus, 1921 (1922) P. 140

Ann. de la Soc. Scient de Bruxelles 1922 p. 338

X-rays by Kaye p. 268

Bragg - X-ray and Crystal Structure, p. 297.

Proc. Roy. Soc., 1921, 29 p. 261.

Phil. Mag. 27, p. 320, 1914.

Phys. Rev. 8, 528 (1916)

The Theory of Electrons, 2nd Ed., p. 149.

Sc. Am. Sept. 1923.

Bragg - X-rays and Crystal Structure p. 295.